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Phase Behaviour of Blends with Mesophase Components

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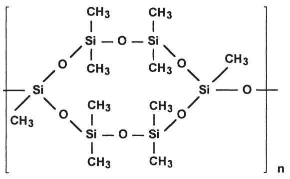
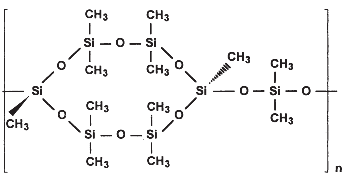
Summary: Temperature transitions and structural transformations were studied for blends of two thermotropic mesophase cyclolinear polymethylsiloxanes with linear PDMS of various molecular weights by means of DSC, optical polarizing microscopy, and optical interferometry. Compatibility of the components which depends on the chemical structure of cyclolinear polymethylsiloxanes, molecular weight of PDMS, composition, and temperature affect formation of mesophase in cyclolinear polymethylsiloxanes. The most interesting aspect of the phase behaviour consists in the fact that it is possible to reach compatibility of the components in the mesomorphic state for the blends of two cyclolinear polymethylsiloxanens due to various annealing regimes in one-phase molten state.

Introduction.

For further insight into our knowledge about mesophases, it is of interest to study the formation of the mesophase in polymer blends, one or both of whose components fall into category of thermotropic mesophase polymers such as cyclolinear polymethylsiloxanes (P). The objective of this work was to study the temperature transitions in the blends of P-1 and P-2 (cyclolinear polymethylsiloxanes)



P-1



P-2

with linear PDMS of various molecular weights and in the P-1/P-2 blends.

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P-1 is an atactic polymer (the degree of polycondensation n = 32, M_w =17 000, and M_w/M_n = 3.7), which exists in the mesomorphic state in the temperature range extending from the glass transition temperature T_g = -90°C to the isotropization temperature T_i = 250°C [1]. P-2 is a *trans* tactic polymer (the content of the *trans* form is more than95%, n = 100, M_w = 51 000, M_w/M_n = 2.1, and T_g = -90°C), which exists in the mesomorphic state in the temperature range extending from the melting temperature T_m = 10°C to T_i = 93°C [1]. Three linear PDMS were used as the components of the blends. PDMS-600: M_w = 600, M_w/M_n = 1.1, and T_g = -130°C; PDMS-5600: M_w = 5600, M_w/M_n = 2.8, and T_g = -120°C. PDMS-44 000:
M_w = 44 000, M_w/M_n = 4.8, and T_g = -120°C.

The P-1/PDMS, P-2/PDMS, and P-1/P-2 blends were prepared by dissolving the polymers in chloroform.

Compatibility of components and formation of the mesophase of Ps.

Blends of P-1 (without a flexible dimethylsiloxane spacer between 6-membered methylsiloxane cycles) and PDMS are characterized by the complete incompatibility of the components at the temperatures below T_i [2]. Therefore, there is no marked effect of PDMS on the formation of the P-1 mesophase (curve 1, Fig.1).

Introduction of the flexible spacer between 6-membered methylsiloxane cycles of P-2 increases the chemical affinity of components in the P-2/PDMS blends resulting in their complete or partial compatibility, depending on the molecular weight and the content of PDMS, as well as the temperature [2]. Curves (2-4) in Fig.1 show the sharp decrease in the heat of isotropization of P-2 mesophase with the increase in the content of PDMS. The DSC data agree with the direct optical microscopic observations. The intensity of light transmission in the crossed polarizers of P-2/ PDMS blends at room temperature decreases with the increase in the content of PDMS. Above the critical content of PDMS, the dark field is observed for these blends. Therefore, there is a considerable effect of the content of PDMS on the formation of the P-2 mesophase in the P-2/PDMS blends.

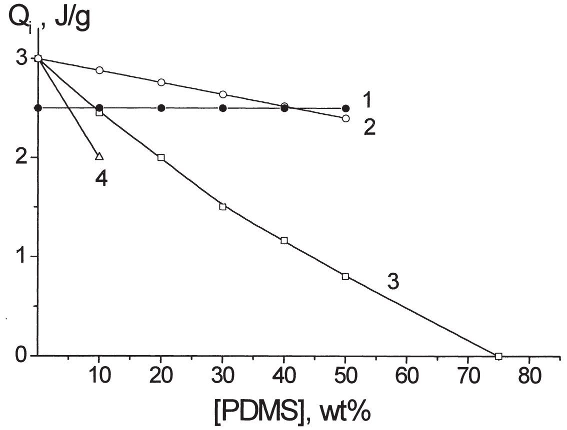

Fig.1: Heat of isotropization, Q_i, of (1) P-1 and (2-4) P-2 mesophases vs. the composition of (1) P-1/PDMS-44000, (2) P-2/PDMS-44000, (3) P-2/PDMS-5600, and (4) P-2/PDMS-600.

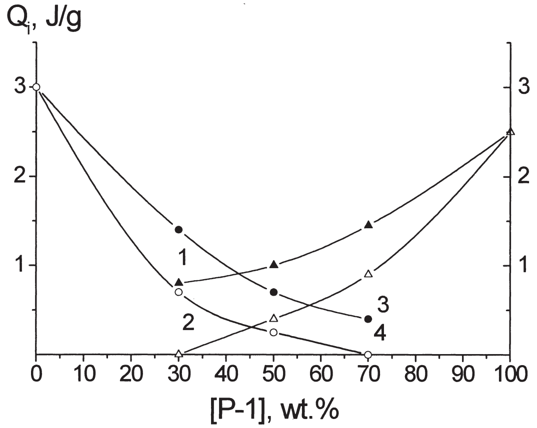

Fig.2: Heat of isotropization (1,2) P-1 and (3,4) P-2 vs. the composition of the P-1/P-2 blend obtained from the common solvent (chloroform) (1,3) and (2,4) after annealing at 280°C for 40 min.

It is known from the literature that isomorphism is a rather rear phenomenon for crystalline polymers [3]. However, because polymers in the mesomorphic state is usually less ordered than in crystalline one, it is interesting to clarify if the mesomorphic cyclolinear polymethylsiloxanes with only a slightly different molecular structure are compatible in the mesomorphic state. Systematic study of P-1/P-2 blends of various compositions in a wide temperature range including molten and mesomorphic states have been performed recently [4]. First of all, it has been recognised that in the molten state P-1/P-2 blends are completely compatible for all contents of the components. However, below the T_i of the P-1 the compatibility of the components depends on the composition, temperature and conditions of preparation of the blends. In particular, Fig.2 shows a strong effect of the composition of the P-1/P-2 blends on the formation of the mesophases in P-1 and P-2. This effect increases after annealing at a temperature above T_i of P-1 (in the isotropic melt). The optical transparency of the annealed P-1/P-2 blends under the crossed polarizers at room temperature is rather lower because of the lower content of P-1 and P-2 mesophases.

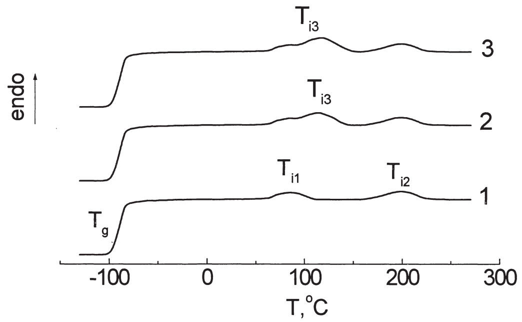

Fig.3. DSC heating traces of the P-1/P-2 (50/50) blend annealed in the isotropic melt at 280°C for 40 min. Measurements were performed (1) immediately after annealing and after prolonged ageing at room temperature for (2) one month and (3) one year.

Fig. 3 shows that on prolonged ageing at room temperature, when the annealed P-1/P-2 blend is almost an isotropic melt with the traces of P-1 and P-2 mesophases, a kinetically hindered development of the mixed mesophase (T_{i3}) of both polymers takes place. The presence of a six-membered methylsiloxane cycle in these polymers plays the decisive role in the development of their mesophases and controls the type of the resultant structure. The introduction of a flexible dimethylsiloxane spacer between the cycles only decreases the isotropization temperature T_{i2} of P-2 as compared with T_{i1} of P-1. Therefore, a similar type of mesophases of P-1 and P-2 allow one to anticipate the development of a mixed mesophase characterized by its own isotropization temperature T_{i3} intermediate between T_{i1} and T_{i2}.

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